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# Thermal polycondensation of hexakis(*p*-acetylphenoxy)-cyclotriphosphazene

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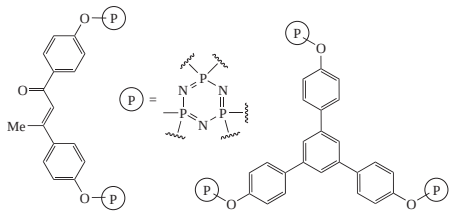
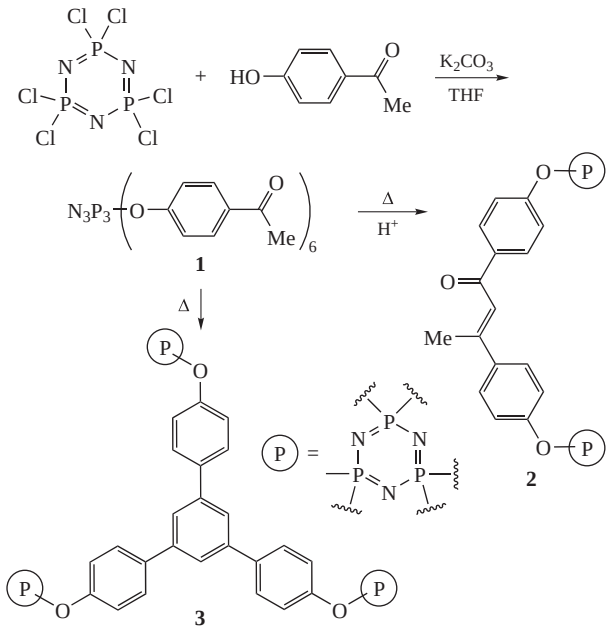
**The thermal polycondensation of acetophenoxy groups in hexakis(*p*-acetylphenoxy)cyclotriphosphazene proceeds in two ways, namely, dimerization and trimerization, to produce chalcone or 1,3,5-triarylbenzene moieties, respectively. The polymers formed in both cases are thermally stable up to 400 °C. The structure of hexakis(*p*-acetylphenoxy)cyclotriphosphazene has been established by X-ray study.**



Functional aryloxyphosphazenes are the unique compounds since they combine organic and mineral nature. The presence of heterocyclic moiety formed by phosphorus and nitrogen atoms in their composition provides the specific physical and chemical properties, such as fireproof,[1] thermal stability,[2] hydrophobicity,[3] bioactivity,[4,5] *etc.* A variation of aromatic substituent groups at the phosphorus atoms in phosphazenes can modify their properties (*i.e.*, making them soluble in water[6] or forming metal complexes[7]). Aryloxyphosphazenes are of special interest in polymer science, since they are capable of altering the rate of decomposition of polylactides,[8] increasing the strength and adhesion of dental materials,[9] improving the resistance of epoxy resins to burning,[10] and forming branched polymers with reduced viscosities of solutions and melts.[11] Moreover, some aryloxyphosphazenes can form polymers characterized by a high thermal stability *via* the condensation of functional groups of aromatic radicals.[12,13] With that knowledge in mind, the present work was aimed at the investigation of possibility of thermal polycondensation of acetylphenoxy-containing aryloxyphosphazene, the evaluation of catalyst effect on the process and structure of condensation products, and the characterization of obtained products.



**Scheme 1**

The possibility of thermal self-condensation was discovered during the thermogravimetric analysis (TGA) of hexakis(*p*-acetylphenoxy)cyclotriphosphazene **1** obtained by the reaction of hexachlorocyclotriphosphazene with *p*-hydroxyacetophenone (Scheme 1).[14]

As one can see in Figure 1(*a*), the rapid loss of mass (~12%) was observed for compound **1** (curve *1*) within the interval of 290–360 °C after that the TGA curve remained on the plateau up to 420 °C.† Meanwhile, the DSC curve (curve *3*)] contained an exothermic peak with its maximum at 320 °C. This behavior may be explained by the rapid progress of some reaction. Taking into account the presence of acetyl groups, aldol condensation may be expected. The second set of TGA experiments was carried out with the addition of 0.5 wt% of *p*-toluenesulfonic acid in order to confirm this hypothesis, since the acid should facilitate the aldol condensation. In this case, the reaction has actually started below 250 °C [Figure 1(*a*), curves *2* and *4*], but the loss of mass upon reaching the plateau was only about 6 wt%.

† The IR spectra were recorded on a Nicolet 380 FTIR spectrometer in the transmission mode for the range of 4000–400 $cm^{-1}$ using the equipment of the Shared Research Center of D. I. Mendeleev University of Chemical Technology of Russia. The TGA experiments were conducted on a Derivatograph-C instrument (MOM, Hungary) under argon using the samples of ~10 mg at the heating rate of 10 deg $min^{-1}$. Differential scanning calorimetry (DSC) measurements were performed using a Mettler-Toledo DSC-822e calorimeter (20 K $min^{-1}$). Small angle X-ray scattering (SAXS) measurements were carried out on an AMUR-K laboratory diffractometer at the CuK$\alpha$ radiation ($\lambda$ = 0.154 nm).

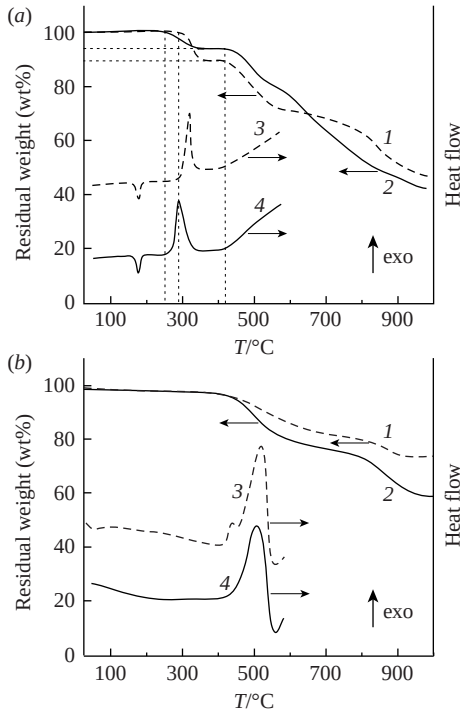



**Figure 1** TGA/DSC curves of (*a*) compound **1** (*1*, *3*) without acid, (*2*, *4*) in presence of 0.5 wt% of *p*-toluenesulfonic acid and (*b*) polymers (*2*, *4*) **2** and (*1*, *3*) **3**.

Therefore, the condensation in the presence of acid proceeds in a different way.

One may assume that polymer **2** (see Scheme 1)‡ can result from aldol condensation process, which is in a good agreement with the TGA data on the sample with the added acid. Once polymer **2** is formed, one molecule of water per two acetophenoxy groups is released (5.7 wt% of compound **1** mass).

The formation of polymer **2** was also confirmed by IR spectroscopy (Figure 2). In addition to the vibrations of methyl (1358 $cm^{-1}$) and carbonyl (1686 $cm^{-1}$) groups, the double bond vibrations appear at 1653 $cm^{-1}$.

The IR spectrum of heated acid-free sample does not contain bands corresponding to carbonyl and methyl groups and double bonds. This fact can be explained by the formation of new

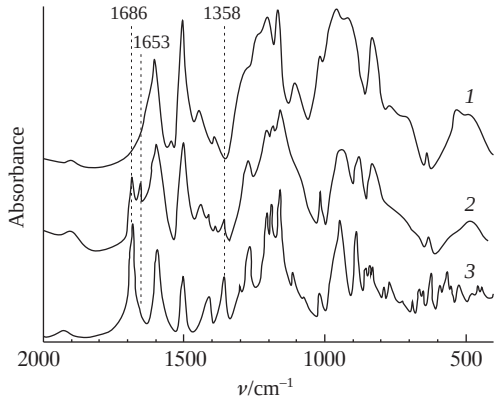



**Figure 2** IR spectra of (*1*) compound **1** and polymers (*2*) **2** and (*3*) **3**.

‡ *Synthesis of* **2** *and* **3**. Two samples (0.3 g each) of compound **1** were grinded in an agate mortar. *p*-Toluenesulfonic acid (1.5 mg) was added to one of them and this was grinded again. The resulting fine powders were compressed into tablets, placed in a ceramic weighing bottles and heated in a muffle furnace in an argon flow (up to 280 °C for the sample with acid and up to 320 °C for the sample without it) at the heating rate of 10 K $min^{-1}$. The samples were then kept at these temperatures for 10 min to give the solid brown (**2**) and black (**3**) polymers.

aromatic ring *via* a condensation of three acetylphenoxy groups. Such trimerization is accompanied by the release of one water molecule per one acetylphenoxy group, which corresponds to the theoretical value of 11.4 wt% and is also in agreement with the TGA data that indicated the weight loss of ~12 wt% for the acid-free condensation of compound **1** [see Figure 1(*a*), curve *1*]. The thus resulting cross-linked polymer can be described by the structural formula **3** (see Scheme 1).‡ Note also that the phosphazene ring was preserved in the both cases of polymer formation, which was confirmed by the presence of IR peaks corresponding to the vibrations of P=N bonds in the region of 1160–1220 $cm^{-1}$.

The observed trimerization of acetylphenoxy groups can be explained by a mobility of aromatic fragments due to the rotation around the Ar–O–P bonds and by the flexibility of phosphazene ring caused by its deformation [*i.e.*, the phosphazene ring in starting $N_3P_3Cl_6$ is flat, but in compound **1** it possesses a twist-bath conformation Figure 3(*c*)]. The flexibility of its molecule was also confirmed by single-crystal X-ray analysis of compound **1**,§ which revealed that the molecules of **1** in the crystal are linked *via* hydrogen bonds forming a dense framework

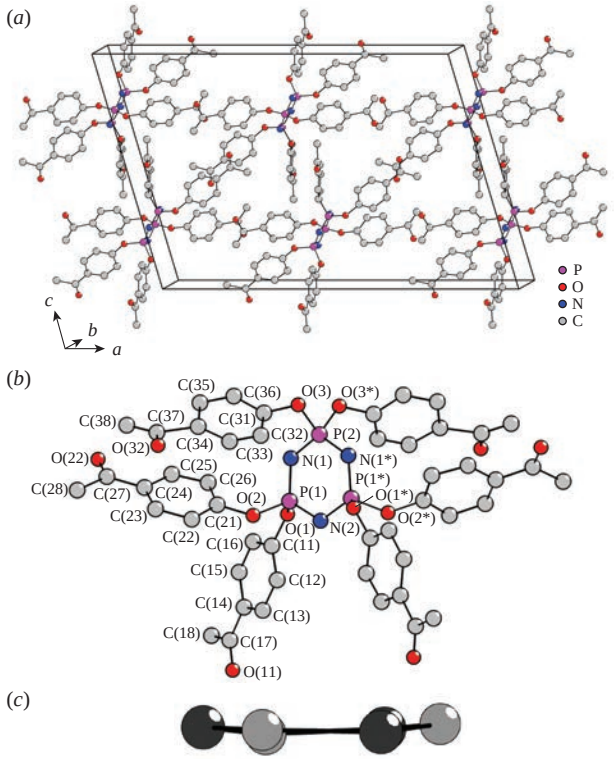



**Figure 3** (*a*) The crystal structure, (*b*) isolated molecule and (*c*) phosphazene ring of compound **1**.

§ *Crystal data for* **1**: $C_{48}H_{36}N_3O_{12}P_3$, $M$ = 939.7, space group $C2/c$, $a$ = 28.851(6), $b$ = 8.0666(7) and $c$ = 19.648(3) Å, $\beta$ = 106.154(2)°, $V$ = 4392.0(8) $Å^3$, $Z$ = 4, $d_{calc}$ = 1.421 g $cm^{-3}$, $\mu$(MoKα) = 0.205 $mm^{-1}$. Total of 48134 reflections were measured (2.16° ⩽ 2$\theta$ ⩽ 30.65°) using a Bruker APEX II diffractometer at 120 K and 6474 unique reflections ($R_{int}$ = 0.2229, $R_\sigma$ = 0.1314) were used in all calculations. The final $R_1$ = = 0.0800 [for 2480 reflections with $I > 2\sigma(I)$] and $wR_2$ = 0.1334 (all data). A structure model was determined by the 'charge flipping' method using the SUPERFLIP computer program.[15] The structure determination and refinement were carried out using the Jana2006 software package.[16] The majority of acetophenyl moieties were disordered, which could be the reason of very weak diffraction at high values of 2$\theta$ angle. Consequently, the *R*-values were fairly high.

CCDC 1580775 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

[Figure 3(*a*)]. These bonds are established between the oxygen atoms of carbonyl groups of one molecule and the hydrogen atoms of methyl groups of other molecules. In this case, all the acetylphenoxy groups are involved in the framework formation. Since the condensation occurs in melt [mp of compound **1** is 170 °C; see Figure 1(*a*), curves *3* and *4*] on heating the mobility of segments of compound **1** is increased promoting the trimerization.

The different formation of polymers **2** and **3** can be caused by the rapid condensation progress in the absence of acid [see Figure 1(*a*), curves *1* and *3*] with the simultaneous participation of all acetyl groups. In the presence of acid, the reaction is slower with the participation of only acid-activated groups. Thus, acid causes the formation of cross-linked polymer containing the β-methylchalcone moieties, while trimerization becomes sterically hindered.

According to small angle X-ray scattering data, both of the polymers are amorphous, but their glass transition temperatures are higher than the temperatures of decomposition [see Figure 1(*b*), curves *3* and *4*].

The obtained polymers remain heat-resistant up to 400 °C and produce the coke residue of 60 wt% (polymer **2**) and 75 wt% (polymer **3**) upon heating to 1000 °C [see Figure 1(*b*), curves *1* and *2*]. Polymer **3** containing benzene-1,3,5-triyl moieties is of considerable interest as the organic-inorganic high-temperature material for various areas of science and technology.[17–19] In addition, the prepared polymers can be employed for obtaining compositions with reduced combustibility due to the presence of phosphazene.

In conclusion, this work revealed the two ways of thermal polycondensation of hexakis(*p*-acetylphenoxy)cyclotriphosphazene, providing two different polymers. The reported polymers can be promising materials for various applications due to their properties caused by the presence of phosphazene ring.

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## References

1 J. Wang, X. Su and Z. Mao, *Polym. Degrad. Stab.*, 2014, **109**, 154.
2 L. Qian, L. Ye, Y. Qiu and S. Qu, *Polymer*, 2011, **52**, 5486.
3 X. Huang, W. Wei, H. Wei, Y. Li, X. Gu and X. Tang, *J. Appl. Polym. Sci.*, 2013, **130**, 248.
4 G. Mutwiri, P. Benjamin, H. Soita, H. Townsend, R. Yost, B. Roberts, A. K. Andrianov and L. A. Babiuk, *Vaccine*, 2007, **25**, 1204.
5 R. U. Khan, L. Wang, H. Yu, Zain-ul-Abdin, M. Akram, J. Wu, M. Haroon, R. S. Ullah, Z. Deng and X. Xia, *Russ. Chem. Rev.*, 2018, **87**, 109.
6 M. L. Stone, A. D. Wilson, M. K. Harrup and F. F. Stewart, *Desalination*, 2013, **312**, 130.
7 V. Chandrasekhar and R. S. Narayanan, *Dalton Trans.*, 2013, **42**, 6619.
8 W. Yuan, L. Zhu, X. Huang, S. Zheng and X. Tang, *Polym. Degrad. Stab.*, 2005, **87**, 503.
9 V. V. Kireev, E. M. Chistyakov, S. N. Filatov, A. S. Tupikov, D. V. Panfilova and A. I. Chetverikova, *Russ. J. Appl. Chem.*, 2015, **88**, 866 (*Zh. Prikl. Khim.*, 2015, **88**, 826).
10 H. Liu, X. Wang and D. Wu, *Thermochim. Acta*, 2015, **607**, 60.
11 K. Miyata, Y. Watanabe, T. Itaya, T. Tanigaki and K. Inoue, *Macromolecules*, 1996, **29**, 3694.
12 E. M. Chistyakov, V. V. Kireev, S. N. Filatov, I. V. Terekhov, M. I. Buzin and L. I. Komarova, *Polym. Sci., Ser. B*, 2012, **54**, 407 (*Vysokomol. Soedin., Ser. B*, 2012, **54**, 1330).
13 B. Bing and B. Li, *Sci. China, Ser. B*, 2009, **52**, 2186.
14 E. Çil, M. Arslan and A. O. Görgülü, *Polyhedron*, 2006, **25**, 3526.
15 L. Palatinus and G. Chapuis, *J. Appl. Crystallogr.*, 2007, **40**, 786.
16 V. Petříček, M. Dušek and L. Palatinus, *Jana2006 Software Package*, Institute of Physics, Praha, Czech Republic, 2006.
17 X. Zhang, T. Higashihara, M. Ueda and L. Wang, *Polym. Chem.*, 2014, **21**, 6121.
18 E. M. Maya, E. Rangel-Rangel, U. Díaz and M. Iglesias, *J. $CO_2$ Util.*, 2018, **25**, 170.
19 D. M. Ilgach, G. I. Nosova, T. N. Kopylova, E. N. Nikonova, R. M. Gadirov, R. Yu. Smyslov, L. S. Litvinova and A. V. Yakimansky, *Mendeleev Commun.*, 2017, **27**, 357.

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